

## DIATOMIC MOLECULES ACCORDING TO THE WAVE MECHANICS. II. VIBRATIONAL LEVELS

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The combination of the energy of repulsion and the electronic energy can be considered as a nuclear potential energy

$$E(r) = (e^2 Z_1 Z_2 / r) - V_e(r).$$

The wave function  $\Psi$  can be considered as a product of three factors  $\Psi = N \cdot \Phi(\phi) \cdot \Theta(\theta) \cdot R(r)/r$ , where it can be shown that

$$\Phi = e^{ig\phi}$$

$$\Theta = \sin^g \theta \cdot P_j^g(\cos \theta)$$

where  $g$  and  $j$  are integers. The normalizing factor  $N$  is adjusted so that  $\int \Psi \cdot \bar{\Psi} dv = 1$ .

When these functions have been substituted in the general equation an equation for  $R$  results,

$$\frac{d^2 R}{dr^2} + \frac{j(j+1)R}{r^2} + \frac{8\pi^2\mu}{h^2} [W - E(r)] R = 0. \quad (2)$$

We must search, then, for a form for  $E$

exactly give the allowed energy levels as the finite polynomial.

$$W(n) = -D + h\omega_0 \left[ \left( n + \frac{1}{2} \right) - x \left( n + \frac{1}{2} \right)^2 \right].$$

## A SOLUTION OF THE PROBLEM

The function which it is proposed to use here is the simple one

$$E(r) = D e^{-2a(r-r_0)} - 2D e^{-a(r-r_0)}. \quad (4)$$

If this form of  $E$  is substituted in Eq. (3),  $j$  set equal to zero, and the transformation  $u = (r - r_0)$  made, then

$$\frac{d^2 R}{du^2} + \frac{8\pi^2\mu}{h^2} [W - D e^{-2au} + 2D e^{-au}] R = 0. \quad (6)$$

$$W(n) = -D + h\omega_0(n + 1/2) - (h^2\omega_0^2/4D)(n + 1/2)^2$$

quanta (III, 93) is given very closely by the *area under the  $\Delta G$  curve*. For a linear  $\Delta G$  curve this relation holds exactly and, as can easily be seen, leads also to equation (III, 97).

The foregoing considerations regarding the limit of the vibrational terms are not of great importance for infrared spectra, since the intensity in a series of bands falls off so rapidly that high  $\nu$  values are never observed in practice. However, these considerations will prove to be very important in the discussion of electronic band spectra and of the band-spectroscopic determination of heats of dissociation (Chapter VII).

**Mathematical representation of the potential curves.** As previously mentioned an expression with quadratic and cubic terms in  $(r - r_e)$  [equation (III, 71)] represents the potential energy of a diatomic molecule near the equilibrium position only. A mathematical expression that actually represents a potential curve of the form of the solid curve in Fig. 46, even for large values of  $r$ , has been proposed by Morse (504). It is

$$U(r - r_e) = D_e(1 - e^{-\beta(r-r_e)})^2 \quad (\text{III, 98})$$

Here  $D_e$  is the dissociation energy, referred to the minimum (see Fig. 50), and  $\beta$  is a constant whose value will be derived. It can be seen that the Morse function gives a curve of the form shown in Fig. 46, since, for  $r \rightarrow \infty$ ,  $U$  approaches  $D_e$  and for  $r = r_e$ ,  $U$  is a minimum—namely,  $U = 0$ . On the other hand, for  $r = 0$ ,  $U$  does not approach  $\infty$ , as it must do for a correct potential energy function. However, the part of the curve in the neighborhood of  $r = 0$  is of no practical importance.

Morse has shown that when (III, 98) is substituted for  $V$ , the wave equation (I, 12) can be solved rigorously [see, however, ter Haar (1014)]. The term values are found to be

$$G(v) = \beta \sqrt{\frac{D_e h}{2\pi^2 c \mu}} (v + \frac{1}{2}) - \frac{h\beta^2}{c 8\pi^2 \mu} (v + \frac{1}{2})^2 \quad (\text{III, 99})$$

without any higher powers of  $(v + \frac{1}{2})$ . According to (III, 74), the coefficient of  $(v + \frac{1}{2})$  is  $\omega_e$ . Therefore

$$\beta = \sqrt{\frac{2\pi^2 c \mu}{D_e h}} \omega_e = 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu_A}{D_e}}, \quad (\text{III, 100})$$

where  $\mu_A$  is the reduced mass in atomic-weight units (Aston scale) and  $D_e$  is in

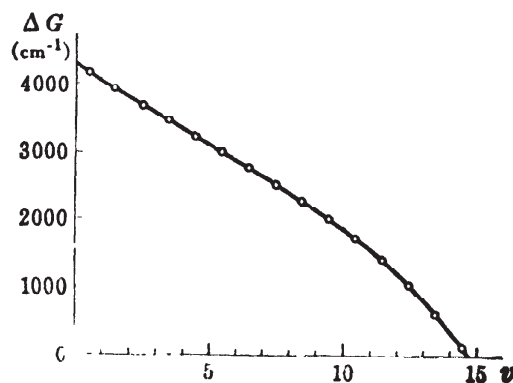


FIG. 51.  $\Delta G$  Curve for the Ground State of the  $\text{H}_2$  Molecule [after the Data Given by Beutler (91)]. The observed  $\Delta G_{v+\frac{1}{2}}$  values are plotted with the abscissae  $v + \frac{1}{2}$ .

$\text{cm}^{-1}$  units. The same formula results from the coefficient of  $(v + \frac{1}{2})^2$  in (III, 99) when (III, 97) is substituted.

The Morse function (III, 98) is frequently used for the representation of potential curves, since it is very convenient. In cases in which the vibrational levels cannot be represented by a two-constant formula, it is best to take the empirical  $D_e$  and  $\omega_e$  in order to calculate  $\beta$  from (III, 100). However, the coefficient of  $(v + \frac{1}{2})^2$  in (III, 99) will then not agree with the observed  $\omega_e x_e$ .

Poeschl and Teller (568) have shown that for a given observed set of vibrational levels the Morse function is not the only possible potential function that, on substitution in the wave equation, will yield these vibrational levels, even if the levels can be represented by a two-constant formula. In order to avoid ambiguity in the choice of the potential function, data on the rotational constants of the molecule must be used. Various authors have given potential functions that take account of the values of the rotational constants. Critical summaries of and improvements upon all this work have been given by Hylleraas (351), Coolidge, James, and Vernon (162a), and Hulburt and Hirschfelder (1078). The last-named authors have suggested the following modification of the Morse function:

$$U(x) = D_e[(1 - e^{-\beta x})^2 + c\beta^3 x^3 e^{-2\beta x}(1 + b\beta x)] \quad (\text{III, 101})$$

In this equation  $x = r - r_e$  and  $\beta$  is given by (III, 100) (our  $x$  and  $\beta$  are defined differently from those of Hulburt and Hirschfelder);  $c$  [not to be confused with the velocity of light occurring in (III, 100)] and  $b$  are constants depending on the vibrational and rotational constants in the following way:

$$c = 1 - \frac{1}{\beta r_e} \left( 1 + \frac{\alpha_e \omega_e}{6B_e^2} \right)$$

$$b = 2 + \frac{1}{c} \left[ \frac{7}{12} - \frac{1}{\beta^2 r_e^2} \left( \frac{5}{4} + \frac{5\alpha_e \omega_e}{12B_e^2} + \frac{5\alpha_e^2 \omega_e^2}{144B_e^4} - \frac{2\omega_e x_e}{3B_e} \right) \right] \quad (\text{III, 102})$$

where the rotational constants  $B_e$  and  $\alpha_e$  will be defined in subsection (c) below. The advantage of the function (III, 101) is that its five parameters can be obtained fairly readily from just those five spectroscopic constants  $\omega_e$ ,  $\omega_e x_e$ ,  $D_e$ ,  $B_e$  and  $\alpha_e$  that are the only ones experimentally determined for most electronic states. Hulburt and Hirschfelder have given the values of the constants  $c$  and  $b$  for the ground states of a considerable number of molecules.

Klein (404) and Rydberg (608) (609) have given a method for constructing the potential curve point for point from the observed vibrational and rotational levels without assuming an analytical expression for the potential function. The exact curves obtained in this way are generally fairly closely approximated by the simple Morse curve (which is much simpler to calculate). The potential curve for the ground state of  $\text{H}_2$  in Fig. 50 (full curve) has been derived by the Klein-Rydberg method. The corresponding Morse function is given as a broken-line curve [see also Hylleraas (351)]. In many cases the agreement is not quite as good. Nevertheless for many considerations the Morse function is a fairly satisfactory approximation. A very much closer approximation to the "exact" curves is provided by the modified Morse function (III, 101) at least in all cases in which a comparison has been made. For a discussion of the limitations of the Klein-Rydberg method as well as other important remarks on potential functions reference should be made to the paper by Coolidge, James, and Vernon (102a) which contains also another modification of the Morse function which has considerable merit. Rees (1343) has given an analytical formulation of the Klein-Rydberg method.

Linnett (1175) has suggested a potential function

$$U(r) = \frac{a}{r^m} - be^{-nr}$$

where the first term represents the repulsion of the atomic cores and the constants  $a$  and  $m$  ( $\approx 3$ ) in it are the same for all states of a given molecule, while the constants  $b$  and  $n$  of the second term may be adjusted for each individual state. Linnett has shown that this function gives a better representation of the interrelation of the constants  $k_r$ ,  $r_e$ ,  $D$ , and  $\omega_r x_c$  than does the Morse function. However he has not compared this function with "true" potential functions obtained, for example, by the Klein-Rydberg method.

### (b) The Nonrigid Rotator

**Energy levels.** Thus far we have used the models of the rigid rotator and the harmonic (or anharmonic) oscillator independently of each other. However, it is quite obvious that the molecule cannot be a strictly rigid rotator when it is also able to carry out vibrations in the direction of the line joining the two nuclei. Therefore a better model for representing the rotations of the molecule is given by the nonrigid rotator—that is, a rotating system consisting of two mass points which are not connected by a massless rigid bar but by a massless spring.

In such a system as a result of the action of centrifugal force, the internuclear distance, and consequently the moment of inertia, increases with increasing rotation. Therefore, in expression (III, 15) for the rotational term values of a rigid rotator the factor  $h/8\pi^2 cI$  depends on the rotational energy (that is, on the rotational quantum number), decreasing with increasing  $J$ . A more detailed calculation shows as indicated below that, to a very good approximation, the rotational terms of the nonrigid rotator are given by

$$F(J) = \frac{E_r}{hc} = B[1 - uJ(J+1)]J(J+1). \quad (\text{III, 103})$$

That is to say,  $B[1 - uJ(J+1)]$  appears in the place of  $B$  in (III, 15). The constant  $B$  in (III, 103) is given by the same formula (III, 16) as previously but substituting for the moment of inertia  $I$  its value for zero rotational energy;  $u$  is very small compared to 1. Equation (III, 103) is usually written

$$F(J) = BJ(J+1) - DJ^2(J+1)^2. \quad (\text{III, 104})$$

It should be noted that some authors use a positive sign in (III, 104) instead of the negative one used here. With our choice of sign  $D$  always has a positive value.<sup>9</sup>

(The rotational constant  $D$  depends on the vibrational frequency  $\omega$  of the molecule, since the smaller  $\omega$  is, the flatter will be the potential curve [according to (III, 31)] in the neighborhood of the minimum and therefore the greater will be the influence of centrifugal force—that is, the greater will be  $D$ . It will be shown below that  $D$  is given by

$$D = \frac{4B^3}{\omega^2} \quad (\text{III, 105})$$

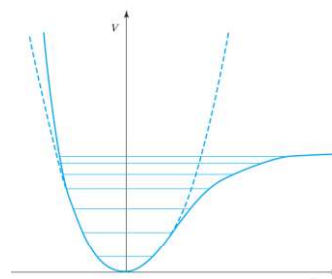
if, for the vibrations, the model of the harmonic oscillator is used. As we have

<sup>9</sup> This  $D$ , of course, has nothing to do with the dissociation energy  $D$ .

# ESPECTROSCOPIA MOLECULAR I, QFL-5621

## EXERCÍCIO 2

A figura ao lado com as curvas de energia potencial harmônica e anarmônica, e os níveis de energia do oscilador anarmônico, é tradicionalmente mostrada em livros-texto de Físico-Química.



Use uma planilha eletrônica para fazer uma figura análoga com unidades nos eixos de distância (Å) e de energia (kJ/mol) com as constantes moleculares experimentais da tabela abaixo. Na figura deve constar: a energia potencial e níveis de energias do modelo harmônico, e a energia potencial e níveis de energias do modelo anarmônico de acordo com o potencial de Morse. Faça uma figura para a molécula  $N_2$  e outra para  $I_2$ . Compare o erro no termo anarmônico  $\nu_e x_e$  dado pelo modelo de Morse e os valores experimentais da tabela para  $N_2$  e  $I_2$ .

**Table 4.1 Molecular Constants for Some Diatomic Molecules<sup>a</sup>**

Molecule	Electronic Term	$R_e$ (Å)	$k_e$ (mdyn/Å)	$\tilde{\nu}_e$ (cm <sup>-1</sup> )	$D_e/hc$ (cm <sup>-1</sup> )	$\tilde{B}_e$ (cm <sup>-1</sup> )	$\tilde{\alpha}_e$ (cm <sup>-1</sup> )	$\tilde{\nu}_e x_e$ (cm <sup>-1</sup> )	$\tilde{D}_e$ (cm <sup>-1</sup> )
H <sub>2</sub>	$X^1\Sigma_g^+$	0.7412	5.756	4403.2	38,297	60.85	3.06	121.3	$4.7 \times 10^{-2}$
HF	$X^1\Sigma^+$	0.9168	9.659	4138.7	49,314	20.956	0.796	90.0	$2.2 \times 10^{-3}$
N <sub>2</sub>	$X^1\Sigma_g^+$	1.0977	22.94	2358.0	79,868	1.998	0.0177	14.1	$5.7 \times 10^{-6}$
CO	$X^1\Sigma^+$	1.1283	19.018	2169.8	90,542	1.93127	0.01751	13.294	$6.20 \times 10^{-6}$
CO	$d^3\Delta$	1.3700	5.366	1152.6	29,522	1.3099	0.0168	7.281	$5.8 \times 10^{-6}$
O <sub>2</sub>	$X^3\Sigma_g^-$	1.2074	11.766	1580.2	42,046	1.4456	0.0158	12.0	$4.8 \times 10^{-6}$
I <sub>2</sub>	$X^1\Sigma_g^+$	2.667	1.720	214.52	12,560	0.03739	0.00012	0.61	$4.5 \times 10^{-9}$

<sup>a</sup> Data mainly from *Bourcier*. The isotopic species are <sup>1</sup>H, <sup>19</sup>F, <sup>14</sup>N, <sup>12</sup>C, <sup>16</sup>O, <sup>127</sup>I.